Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

An efficient cyclodepolymerization route for chemical recycling of poly(ethylene adipate)

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EXPERIMENTAL SECTION

Materials. Adipoyl chloride (XiaQing Chemical of Changzhou, 99%) was purified by vacuum distillation, ethylene glycol (Sinopharm Chemical, 98%) was purified by vacuum distillation after being stirred with calcium hydride overnight, pyridine (Qiangsheng Chemical of Suzhou, AR), dichloromethane (Qiangsheng Chemical of Suzhou, AR), tetrahydrofuran (Qiangsheng Chemical of Suzhou, AR) were purified by stirring with calcium hydride overnight and then distilled under nitrogen, ammonium hydroxide (Sinopharm Chemical, 25%~28%), toluene (Qiangsheng Chemical of Suzhou, AR), adipic acid (Zhonghao Chemical of Tangshan, 99.6%), 1,10-decanediol (Aladdin, 98%), dibutyltin oxide (Aladdin, 98%) and titanium tetrabutoxide ($Ti(n\text{-}C4H9O)_4$) (Alfa Aesar, 98%) were used as received.

Instrumentation.

The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on an Agilent Technologies 600/150 MHz DD2 spectrometer with PFG 1H/19F/X probe at 25 °C, using deuterated chloroform as the solvent and tetramethylsilane (TMS) as the internal reference.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass characterization was conducted on a Bruker UltrafleXtreme TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser (355 nm). Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, Aldrich, > 99%) and Sodium trifluoroacetate (CF_3COONa) were served as matrix and cationizing agent, respectively. The sample was conducted in reflectron mode. The data analysis was conducted with Bruker's FlexAnalysis software.

Gel permeation chromatography (GPC) tests were performed on a modular system comprising a Waters 1515 pump, a 2707 plus autosampler, and a 2414 RI detector with three 300 mm (length) × 8 mm (inner diameter) columns including particle size of 10 μm, 6 μm, and 6 μm (PL gel Mixed-C, Polymer Laboratories). $CHCl_3$ was used as mobile phase with a flow rate of 1 mL/min at 35 ºC. All samples were dissolved in $CHCl_3$ with a concentration of 2.0 mg/mL.

Thermogravimetric analysis (TGA) was carried out at a heating rate of 10 K/min from room temperature to 400 ºC under a continuous nitrogen flow of 50 mL/min with a TA Instrument PerkinElmer TGA 4000. The temperature of thermal degradation (T_d) was measured at the point of 5% weight loss relative to the weight at room temperature.

Differential scanning calorimetry (DSC) was performed on a TA Instruments PerkinElmer DSC 8000 within temperature range from - 80 ºC to 100 ºC at a scanning rate of 10 K/min under nitrogen atmosphere with the samples sealed in aluminum pans.

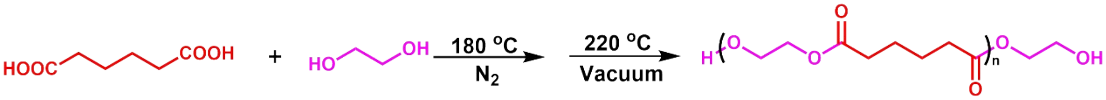
Synthesis of PEA via condensation polymerization

PEA was synthesized according to Scheme S1. Equal amounts of adipic acid and ethylene glycol were charged into a flask and heated to 180 °C with mechanical stirring under N_2. The esterification process was completed after 120 min, then $Ti(n\text{-}C_4H_9O)_4$ (0.02 *wt*%) was added and the temperature was raised to 220 °C to remove excess ethylene glycol. The flask was vacuumed (100 Pa) to perform condensation polymerization, and the polymerization time (typically 90 min) was controlled by the distilled volume of ethylene glycol. The obtained product was characterized by gel permeation chromatography (GPC) and used without further purification.

Synthesis of COEAs via cyclodepolymerization of PEA in toluene

The typical synthetic procedure of COEAs via cyclodepolymerization of PEA in toluene is illustrated as following, using Entry 6 in Table 2 as an example. PEA (10 g), dibutyltin oxide (0.3 g) and toluene (400 mL) were charged into a flask and heated to reflux under magnetic stirring. After 6 h reaction time, the solution was cooled to room temperature and then refrigerated for 12 h. After filtration, the organic layer was washed three times with diluted HCl to get rid of the catalyst, then deionized water and dried with sodium sulfate. Toluene was removed by rotation evaporation, and COEAs were obtained after vacuum dried without further purification. Yield: 24%.

Supporting Scheme and Figures:



Scheme S1. Synthetic route of PEA via traditional condensation polymerization of adipic acid and ethylene glycol.

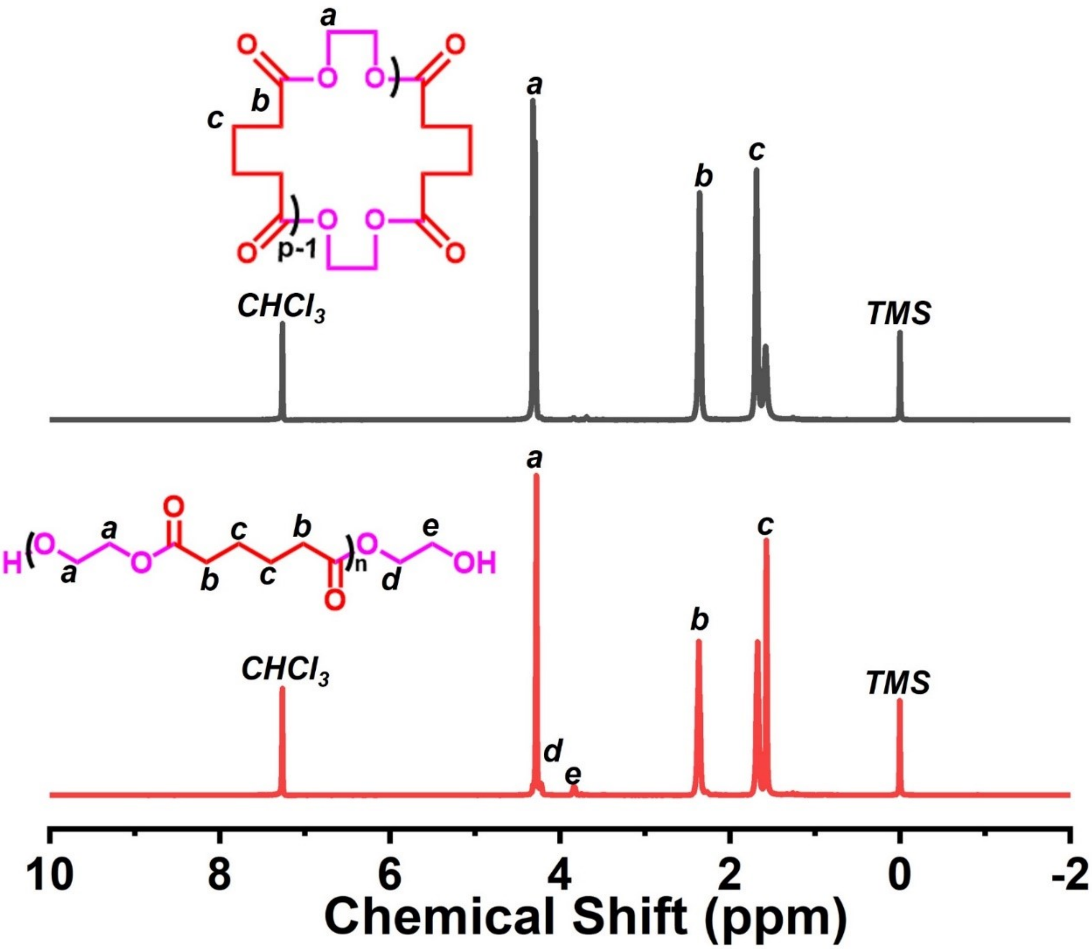


Fig. S1. ^{1}H NMR spectra of COEAs-C and PEA.

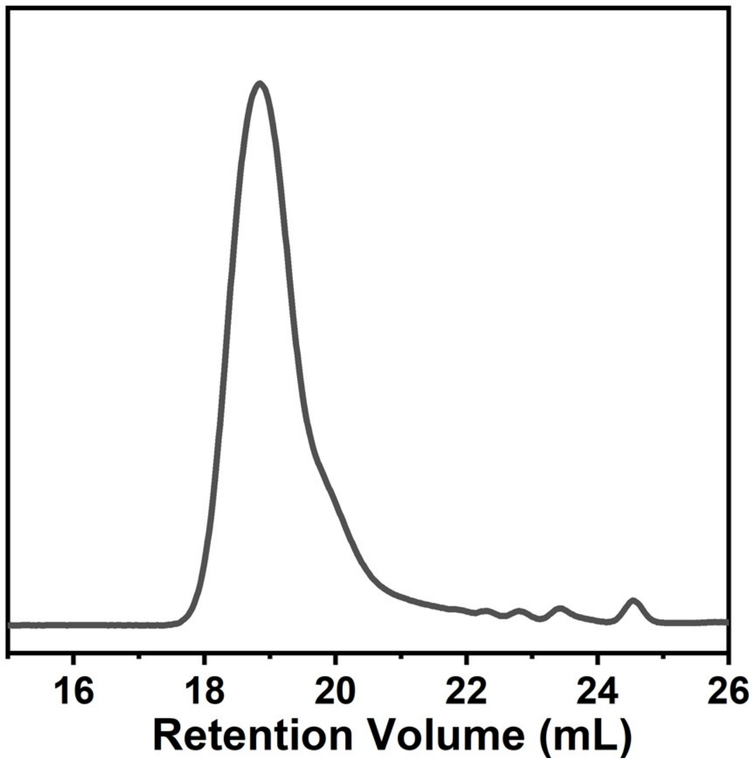


Fig. S2. GPC curves of PEA raw material via traditional condensation polymerization.

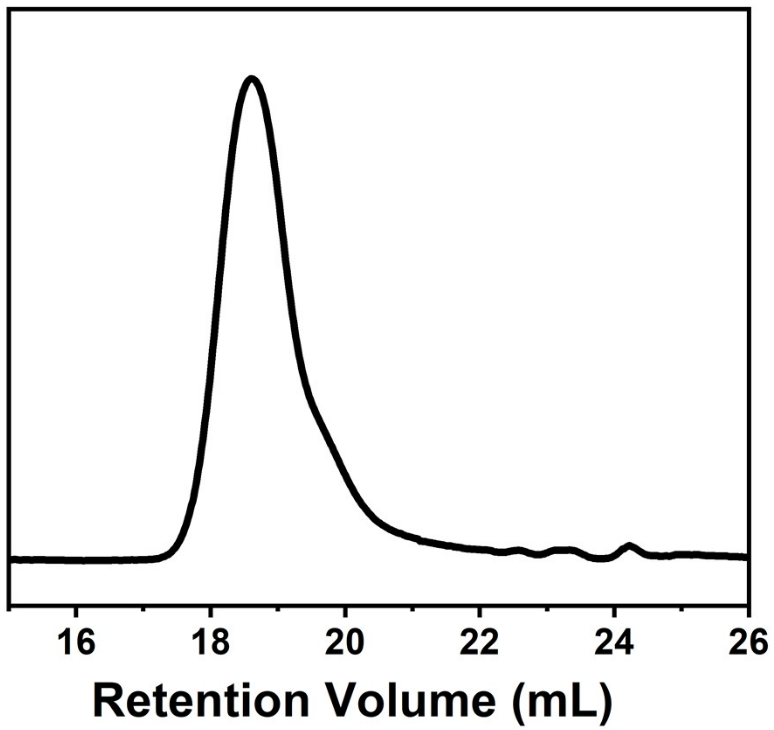


Fig. S3. GPC curve of PEA synthesized via PROP using decanediol and COEAs as monomers.

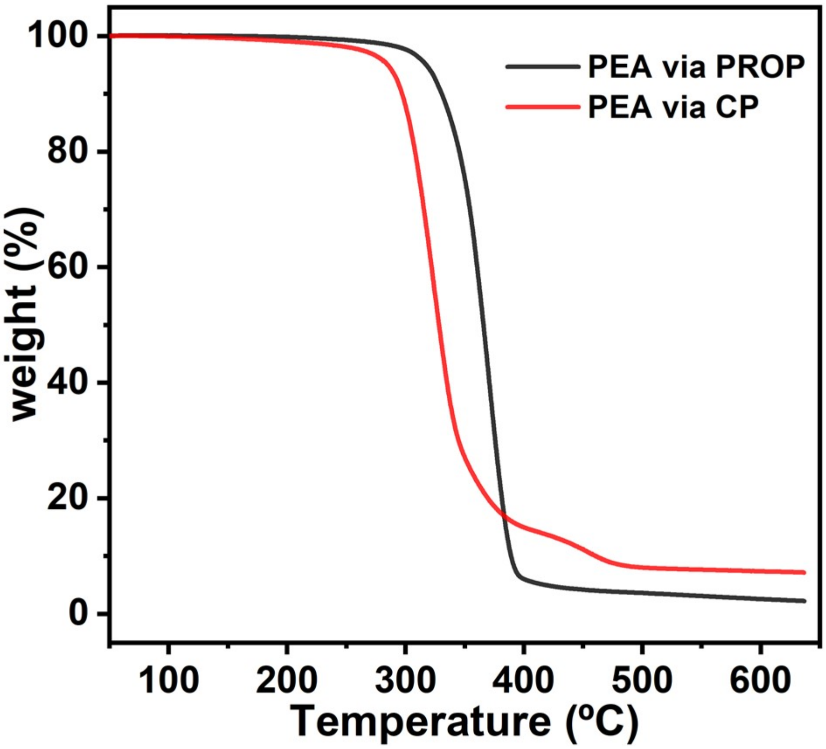


Fig. S4. TGA curves of PEA synthesized via PROP and via CP. Heating rate: 10 K/min under nitrogen.

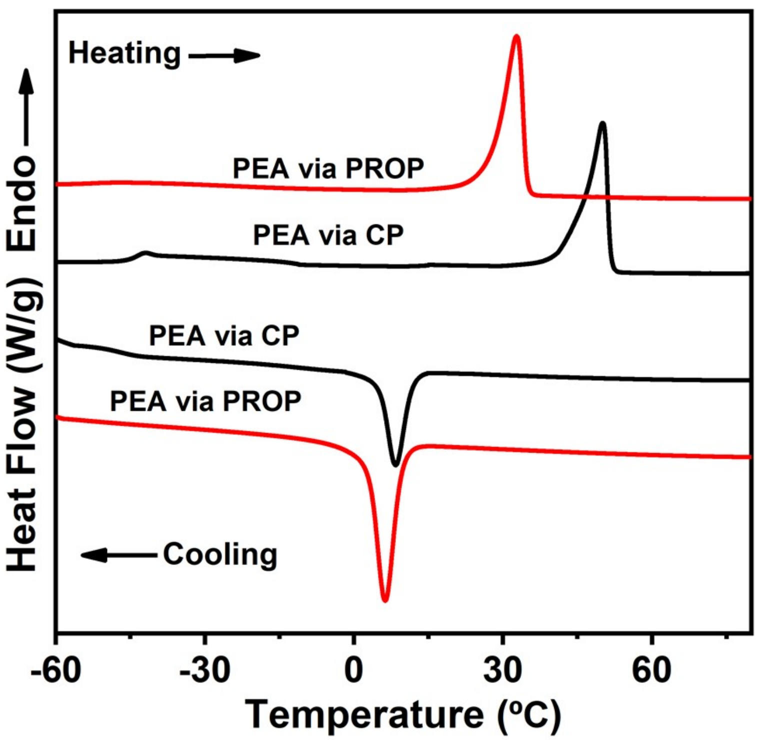


Fig. S5. DSC curves (2nd heating curves and 1st cooling curves) of PEA synthesized via PROP and via CP. Scanning rate: 10 K/min, under nitrogen.